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**EQUILIBRIUM CHEMICAL CHARACTERISTICS
OF NYLON-ACRYLIC ACID GRAFT COPOLYMER**

by

Edward M. Healy, Alvin O. Ramsley
and Basil A. Natsios

July 1969

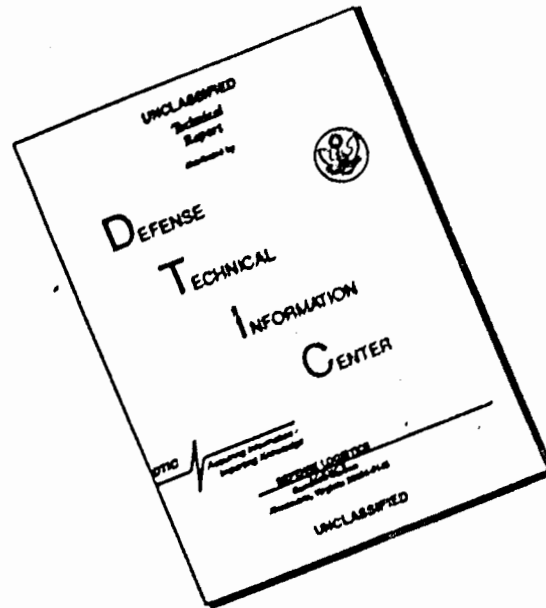
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Clothing & Personal Life Support Equipment Laboratory

C&PLSEL-66

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FOREWORD

The technique of graft copolymerizing functional groups to impart new and useful characteristics to established fibers presents one of the most promising routes to the development of new textile materials.

The graft copolymer studied in the present work offers a high degree of thermal protection in military uniforms. The work reported here covers the first phase of a study of the fundamental chemical characteristics of this fiber, essential to an understanding of the reactions of this representative copolymer, and to the effective utilization of its unique properties.

The work described was carried out in the Textile Dyeing Branch of the Clothing and Personal Life Support Equipment Laboratory, under the In-House Laboratory Initiated Research Program (ILO 1300A91A39). Most of the research was completed in the period from January 1965 to July 1968.

This program was carried out under the direction of Frank J. Rizzo, Chief of the Textile Research and Engineering Division.

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ABSTRACT

The radiation-grafted copolymer of acrylic acid on nylon 6,6-a fiber with flash-resistant properties, was studied as representative of a new and useful class of textile fibers. The present report covers the first phase of research on the fundamental chemical properties of this fiber. Equilibrium characteristics are discussed and results of work on kinetics will follow.

Equilibrium studies were made of rapidly-stirred suspensions of finely cut polymer fiber at several temperatures (30°-60°C). The base-reactive capacity (potassium hydroxide) was 2.0 milliequivalents per gram at 30°C (about twenty times that of the base polymer), with no significant change in capacity at higher temperature.

The acid strength of the copolymer was unexpectedly low (apparent $pK_a=9$), an effect attributed to a heightened polyelectrolyte effect caused by restricted mobility of the carboxyl groups.

Evidence for a conformational transition of the polymer chain at about 55% ionization was shown by a discontinuity in the Henderson-Hasselbach plot of the titration curve. This was attributed to a reversible shifting of the polymer chains.

Neutral electrolyte caused a distinct increase in the apparent acid strength ($pK_a = 5.8$), and a delay in the transition to a point later in the titration (95% neutralized).

No effect of temperature on the equilibrium characteristics of the copolymer was observed.

EQUILIBRIUM CHEMICAL CHARACTERISTICS OF NYLON-ACRYLIC ACID GRAFT COPOLYMER

1. INTRODUCTION

(1)

The graft copolymer of acrylic acid on a nylon 6,6 backbone has been shown to provide significant resistance to thermal radiation when used in suitable textile fabrics. Work on the preparation and characteristics of the calcium derivative of this polymer fiber has been reported earlier.⁽²⁾ The general procedure for preparing the polymer fiber used in the work reported has been reported in the literature^(3,4,5,6) and is outlined below. From the data given in these publications, it is found that a typical product of the radiation grafting of acrylic acid on polyamide fiber would contain half of the original nylon molecules (about 120 units long), carrying side chains of homopolymerized acrylic acid (about 175 units long). The balance of the nylon would appear to be unchanged. Data in the cited literature indicate that such a graft copolymer contains approximately 15-20 percent graft copolymerized polyacrylic acid or about 2.0 milliequivalents of carboxylic groups per gram.^(3, 6)

The physical characteristics of this type of copolymer include increased moisture pickup (compared to nylon itself) and produced a higher melting point. The metallic salt derivatives in particular show a substantial increase in melting point.⁽⁶⁾ The preparation and characteristics of these salts, described briefly in the references cited, are discussed in greater detail elsewhere.⁽²⁾

The work reported covers a study of the equilibrium characteristics of this graft copolymer, particularly in reactions with alkali metal bases. Rate studies are being carried out and will be reported later.

2. OBJECTIVE

The objective of the present study was to determine the chemical reactivity of acrylic acid-modified nylon 6,6 toward acids and bases, and to compare its characteristics with those of related materials such as nylon 6,6 and polyacrylic acid.

3. SCOPE OF WORK AND RESULTS

a. Description of Samples and Procedure

The samples of copolymer studied were prepared by impregnating nylon 6,6 fiber with acrylic acid, exposing it to ionizing radiation, and subsequently removing the ungrafted acid by water extraction.^(3,6)

To facilitate spinning and weaving, the graft copolymer fiber had first been reacted with calcium acetate to form the salt of the acid.⁽²⁾ After the fabric had been woven, it was scoured with non-ionic detergent and heat set (50 sec. at 205°C) to stabilize its structure. The fabric (7.5 oz. poplin) was then reconverted to the acid form by treatment with dilute hydrochloric acid and rinsed thoroughly as described in an earlier report.⁽²⁾ It was then dried at 70°C for two to three hours and stored at 20°C and 40% relative humidity. To minimize diffusion problems during titration, the fabric was cut diagonally into pieces small enough so that the largest segments of yarn were approximately 2mm. long. When a suspension of this material was subjected to high-speed stirring, the pieces of yarn separated almost entirely into short segments of fiber.

In the procedure usually followed, 0.500 g of fiber were added to a one-liter, 3-necked flask containing 500 ml of boiled, distilled water, protected by a stream of nitrogen. A magnetic bar stirrer was driven at high speed by a motor beneath the flask which was immersed in a constant temperature bath maintained at the specified temperature $\pm 0.25^\circ\text{C}$.

Potentiometric titrations were made with a Beckman or Corning combination pH electrode in conjunction with a Beckman Research Model pH Meter readable to 0.005 pH units (reported standard deviation of repeated readings 0.0019 pH). Readings were carried to the third decimal place. The system was found to be extremely sensitive to external electrical influences and to weak convection currents in the test solution. The first difficulty was minimized by the use of large grounded aluminum sheets placed vertically between the operator and the bath containing the electrode assembly. However, even with all stirring stopped for periods up to 60 minutes, the equilibrium pH readings remained unsteady, fluctuating slowly over a narrow range. This instability was attributed to faint convection currents in the test solution, possibly associated with a localized buildup and dissipation of electrolyte as it leaked at a very slow rate from the reference half of the electrode. An inordinately long period of time was thus required for each reading under static (unstirred) conditions and eventually this technique was abandoned. The data reported here are based on readings taken with constant high-speed stirring.*

In many of the experiments, a strip-chart recorder was used to determine when a stable pH was reached (± 0.002 pH units change in 2 minutes). Alternatively, the reaction was continued until a similar steady state was indicated by the null-balance indicator of the pH meter.

In the first experiments, a fresh sample of the copolymer fiber was used for a single equilibrium run. In later experiments, however, successive increments of titrant were added to the reaction mixture, following the

* A report covering the effect of stirring is now in preparation.

attainment of equilibrium at each point. Data obtained by this stepwise procedure fell on the same curves as those from the single-shot procedure; therefore, most of the data given here were obtained by successive additions of base.

b. Theoretical Titration Curve

In addition to the amine and carboxylic acid groups found on the original nylon fiber, the graft copolymer contains additional such groups, added during the grafting process. The final product, therefore, falls in the class of amphoteric fibers. By analogy to other fibers in this group, such as wool⁽⁷⁾, the graft copolymer at its isoelectric point would be expected to carry equivalent numbers of amine and carboxylic acids in the form of dipolar ions (zwitterions). At this point in the titration, the balance of the carboxyl groups would be in the protonated (un-ionized) form.

Data published for the titration of proteins^(9,10,11), wool⁽⁸⁾, and a synthetic polyampholyte⁽¹²⁾ were used as the basis for constructing the theoretical titration curve shown in Figure 1. At the low pH extreme, all of the carboxylic acid groups, all of the amine groups, and probably some of the amide oxygens⁽¹³⁾ would be protonated. As base was added, the highly acidic amide protons would be removed first. During this process, of course, the pH would change but little. When no more of these acidic amide protons remained on the fiber, the pH would change rapidly with small additions of base, and the first plateau shown would result. At this stage in the titration, the amine groups present would remain protonated, while the carboxylic acid groups would be in the un-ionized form, as shown.

Additions of base beyond this point would again cause the curve to drop steeply as protons were removed from the carboxylic acid groups. When the pH reached the isoelectric point, equal numbers of carboxyl groups and amine groups would be present in ionic form. Again the pH would change rapidly with the addition of more base, and a second plateau would result. The capacity of an ampholyte to react with acid may be considered equivalent to the amount of acid added between the two plateaus just described. Although this capacity is determined by the number of amine groups in the molecule, the reaction with acid actually consists of the titration of carboxylate anions which are equivalent in number to the amine groups present in ionic form.

With further addition of base to the reaction mixture, protons would be removed from the remaining carboxylic acid groups, while the pH remained nearly unchanged. A third plateau would be expected when this third class of protons was exhausted, i.e., when all of the carboxylic groups had been converted to the anionic form.

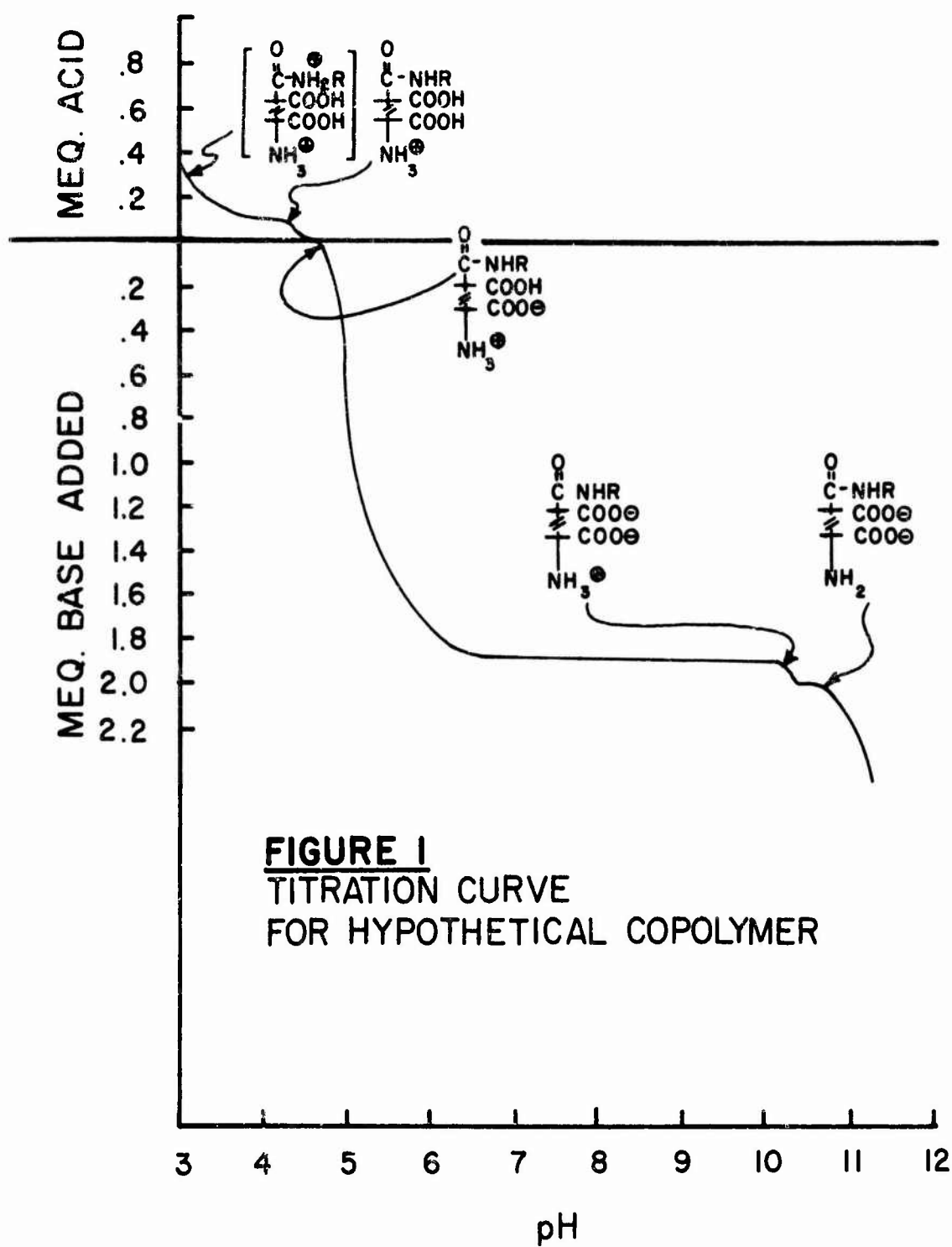


FIGURE 1
TITRATION CURVE
FOR HYPOTHETICAL COPOLYMER

In the last phase of the titration, the curve would again drop sharply as the protons were removed from the protonated amine groups. Eventually, at a high pH, the titration would be complete, and the final plateau shown would result. (The values shown in Figure 1 are those derived later in the present work.)

c. Titration with Base

(1) Base Capacity

Samples (0.5 gm) of fiber, prepared as described in 3a, were suspended in 250 ml. of boiled distilled water being stirred under nitrogen, and maintained at the specified temperature (-0.25°C). After a stable pH reading was obtained for the fiber alone, KOH solution (0.1 N or 0.01 N) was added from a microburet. After each addition, the reaction mixture was allowed to come to equilibrium. At 30°C, this took from 5 to 30 minutes. The individual points thus obtained were plotted as in Figure 2.

With soluble monomeric acids, the end point of a titration would be indicated by a leveling, or a plateau, in the curve. Under the conditions described here, however, an insoluble polymeric acid or a protein would show only an inflection at the end-point.⁽⁸⁾ Figure 2 shows such an inflection in the curve for the acrylic acid-nylon copolymer, titrated with KOH at 30°C. The base capacity indicated (2.0 meq./gm. of fiber) agrees well with that found under other conditions, as described below (3c⁽⁴⁾ and 3c⁽⁵⁾).

(2) Strength of the Copolymer Acid

From the dissociation constant for a weak monomeric acid, the following expression may be derived:

$$\text{pH} = \text{pK}_a + \log\left(\frac{1-\alpha}{\alpha}\right)$$

where α is the fraction of the carboxyl groups which have been ionized.

Titration curves for a number of polymer acids have been found to follow the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_{\text{app}} + n \log\left(\frac{1-\alpha}{\alpha}\right)$$

where n is a constant (the slope of the appropriate curve) and K_{app} is the apparent dissociation constant.

The value of the apparent dissociation constant, then, may be determined from the value of the pH at the point on the curve where $\alpha = 0.5$. In Figure 2, titration curves for a weak monomeric acid, a soluble polymeric acid, and the acrylic acid-nylon graft copolymer are given. The corresponding values for K_{app} are collected in Table I.

TABLE I
APPARENT pKa OF ACIDS

Acetic Acid	4.8
Polyacrylic Acid	6.2
Graft Copolymer	9.0

Since the acid portion of the copolymer consists of homopolymerized acrylic acid⁽³⁾, it might be expected to resemble polyacrylic acid in its chemical properties. However, the distinctly different curves for the two acids (Figure 2) show marked differences.

Consider first the difference in acid strength between a monomeric weak acid, such as acetic, and a polymeric weak acid, such as polyacrylic (Figure 2). The difference between them is generally attributed to the polyelectrolyte effect^(14,15,17); negative charges are introduced in the course of titration of a polymeric acid, which makes the introduction of successive negative charges progressively more difficult. Consequently, the work required to remove additional protons increases as the titration proceeds, and the polymer acid appears weaker than the corresponding monomeric acid. (A somewhat similar earlier explanation of the deviation of the observed from the expected values of acid-base strength of wool is found in the literature⁽¹⁸⁾.)

When the polymeric acid is soluble in water, as polyacrylic acid is, both the backbone chain and the side chains will have considerable freedom of movement. Consequently, the mutual repulsion of the negative charges developing as titration proceeds, will tend to force apart the carboxyl groups and the portions of the backbone chain carrying them, thus minimizing the extra work required by the polyelectrolyte effect.⁽¹⁷⁾ With insoluble compounds of the type described in the present work, however, motion of both the polymer backbone and the side chains is severely restricted, and the polyelectrolyte effect should be very strong. As shown in Figure 2, this is indeed the case, and the nylon-acrylic copolymer behaves as a significantly weaker acid than would be predicted, having a pKa similar to that of phenol (pKa 9).

(3) Effect of Temperature

When titrations of the acrylic acid-nylon graft copolymer with KOH were carried out at 30°C and 50°C, (Figure 3), the equilibrium data points obtained appeared to fall on a single curve. The very small or zero enthalpy change indicated by the results is reasonable for the neutralization of carboxylic acid groups.⁽⁶⁾ The ammonium ion (protonated amine) component of the dipolar ion is present in a much smaller amount than the carboxyl acid groups, and, presumably for this reason, the positive enthalpy change expected from their neutralization was not observed.

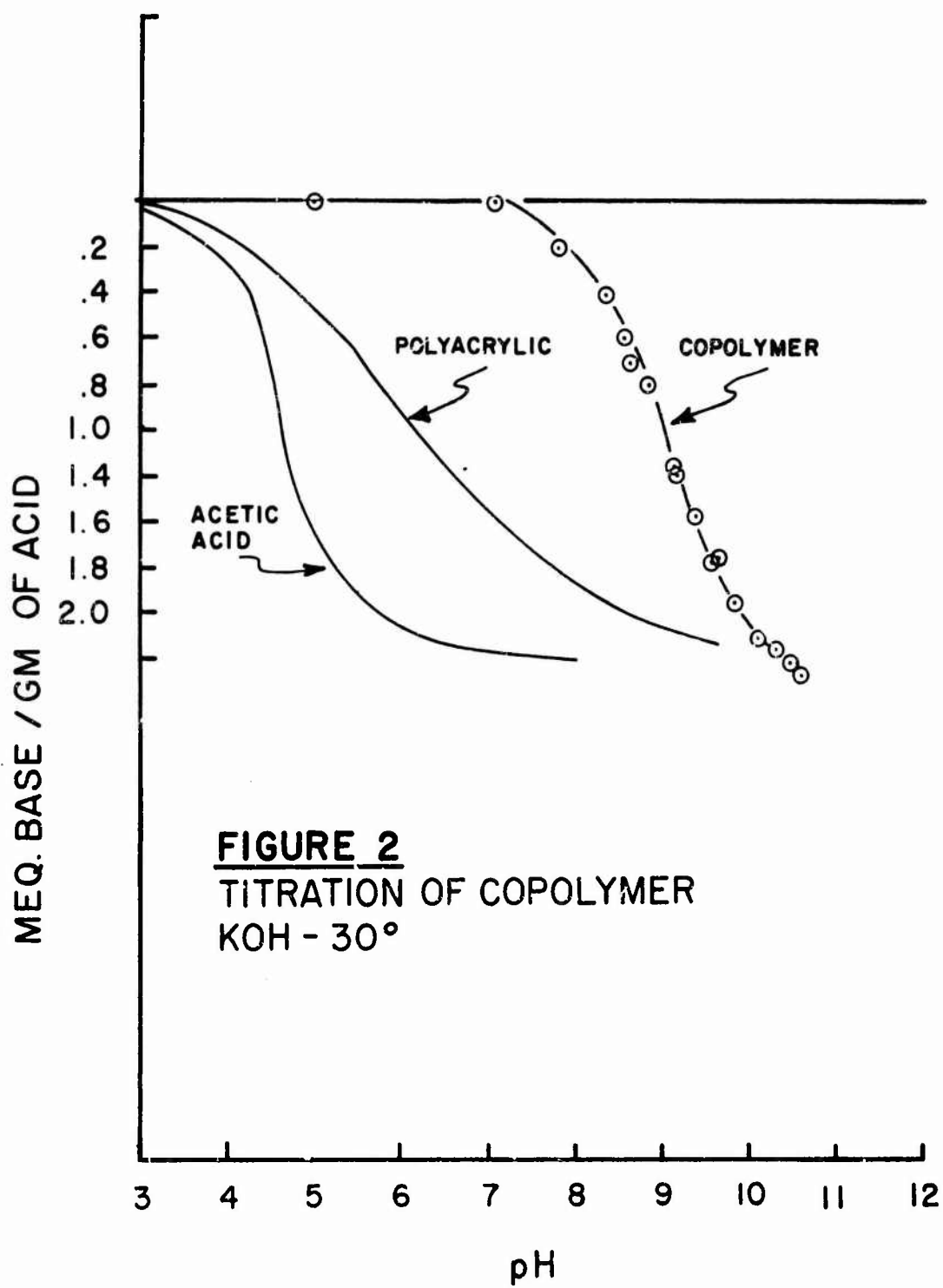


FIGURE 2
TITRATION OF COPOLYMER
KOH - 30°

(4) Effect of Neutral Electrolyte

When the copolymer was back-titrated with HCl (after being titrated with KOH), the resulting equilibrium curve was shifted toward the acid end. Subsequent retitrations of the same mixture gave curves falling progressively even further toward the low pH end of the scale. That this was caused by formation of potassium chloride during the titration was shown by titrating a new sample of copolymer with KOH in the presence of 1M KCl. Under these conditions, the forward and reverse titration curves were superimposed (Figure 4).

The marked effect of potassium chloride in shifting the curves toward the low pH end of the scale may be attributed to suppression of the polyelectrolyte effect.⁽¹⁴⁾ Shielding of the negatively charged carboxylate groups formed during titration permits easier removal of successive protons, and the copolymer thus appears as a much stronger acid. (The apparent pKa is 5.8.)

(5) Titration with Calcium Hydroxide

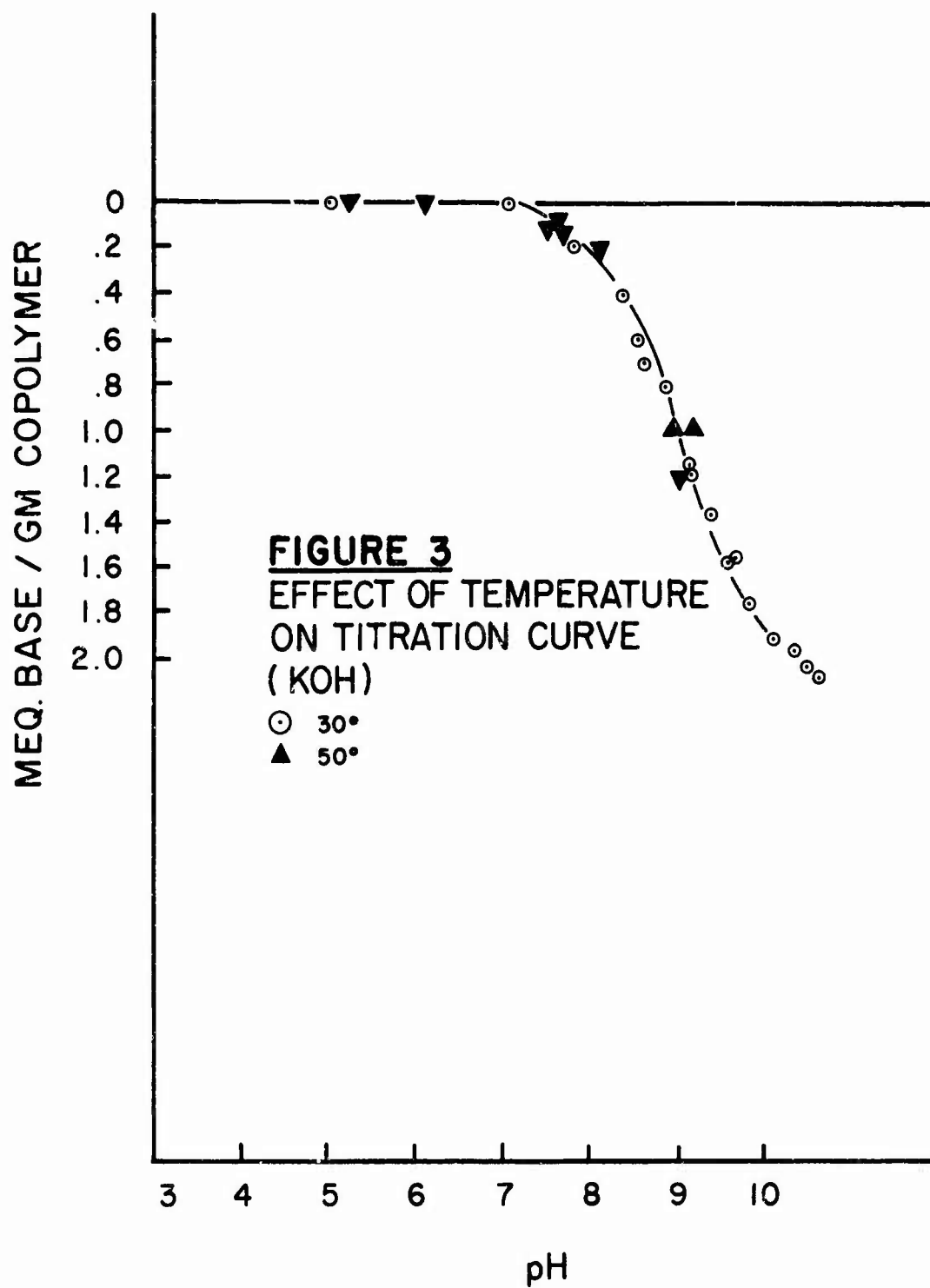
The titration of a highly constrained polymer acid should be strongly influenced by the size and charge of the cation of the base.^(14,19) When the hydroxide of a divalent ion of small ionic radius (calcium) was used, a marked difference was indeed noted. The curve (Figure 5) has again been displaced to the left of the KOH curve showing greater ease of neutralization with the calcium base (pKa = 6.6). However, the effect of the small divalent ion at every point on the curve is less than that resulting from suppression of the polyelectrolyte effect with neutral polyelectrolyte described earlier.

(6) Equilibrium Reversibility

At high pH's, after the fiber has been reacted with base, the copolymer fibers form a swollen, slimy mass. The polymer acid would indeed be expected to swell as far as possible as the anionic carboxyl groups are formed, but it was not clear whether the acid form of the copolymer, regenerated by treating the neutralized form with acid, would show the same equilibrium titration characteristics as the original copolymer fiber.

Fiber was titrated to pH 12 with KOH at 30°C, then back-titrated to pH 5 with HCl. The regenerated acid form thus obtained was washed repeatedly on a suction filter (to remove KCl) until no test for chloride was given by the filtrate. When the fiber was then titrated with KOH again, a curve (Figure 6) was obtained which was superimposable on the original KOH curve.

Reversibility of the titration curve was confirmed by using additional portions of the fiber itself as the acid in the back titration. Data points thus obtained fell on the forward titration curve (Figure 7).



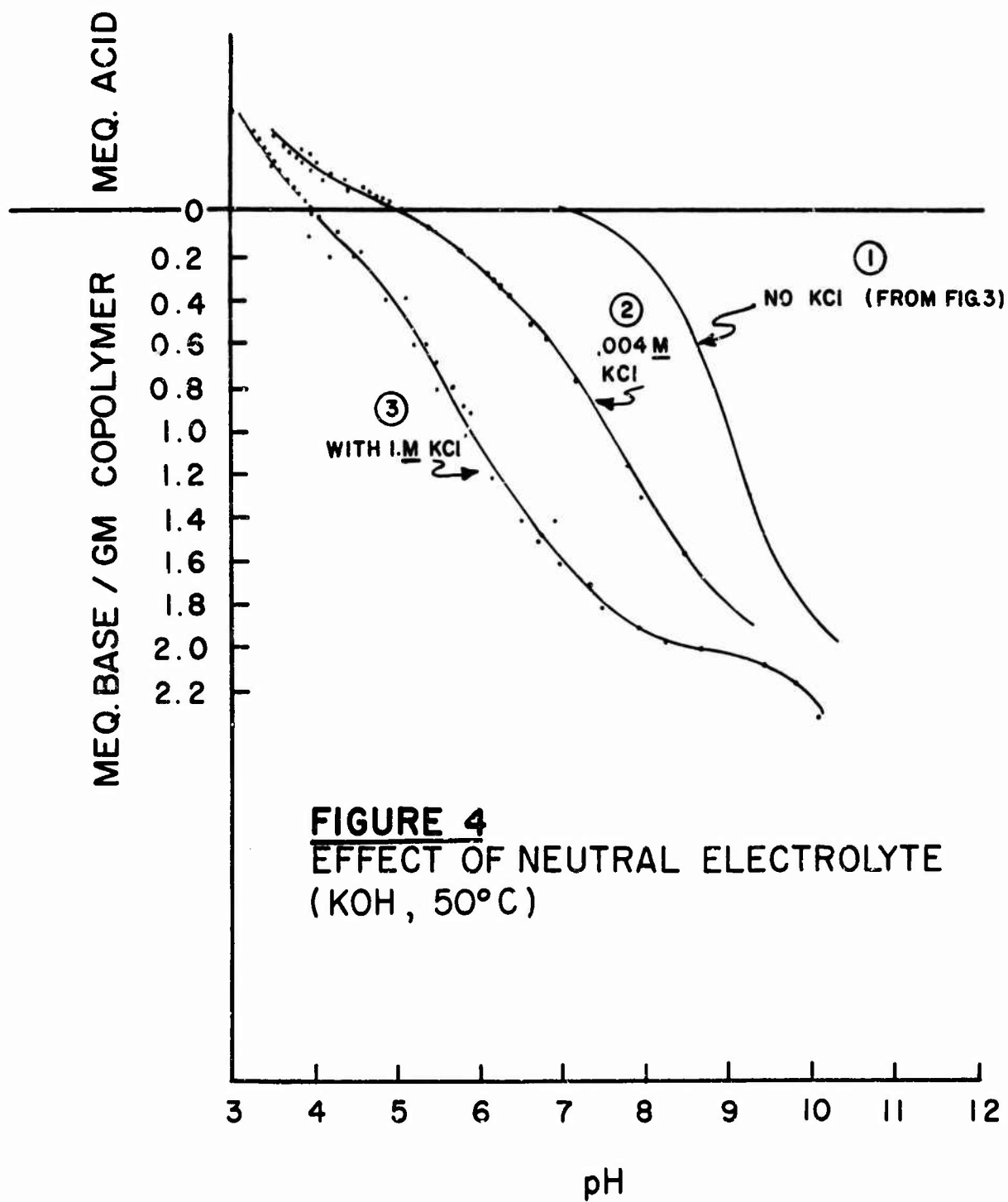
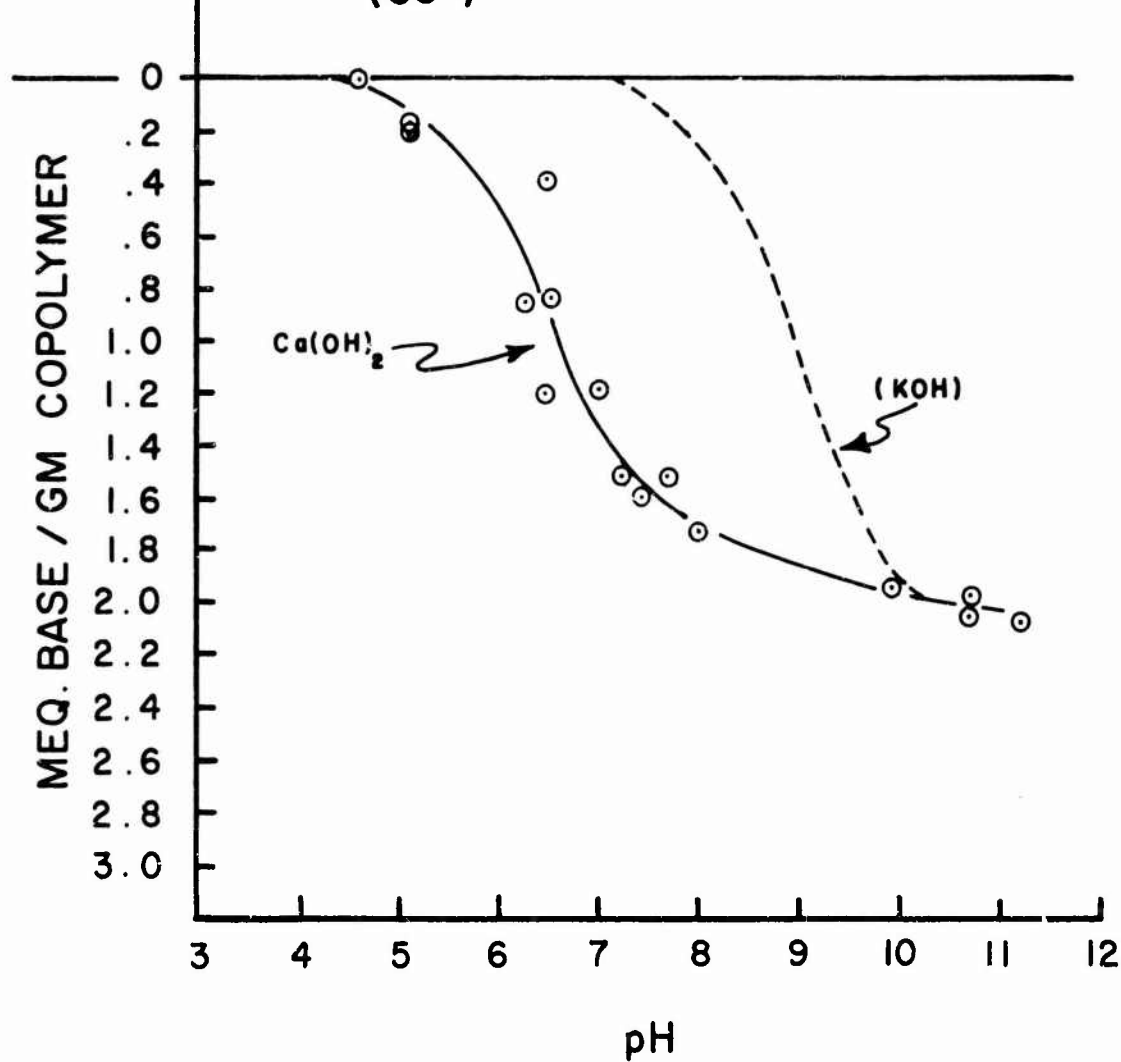
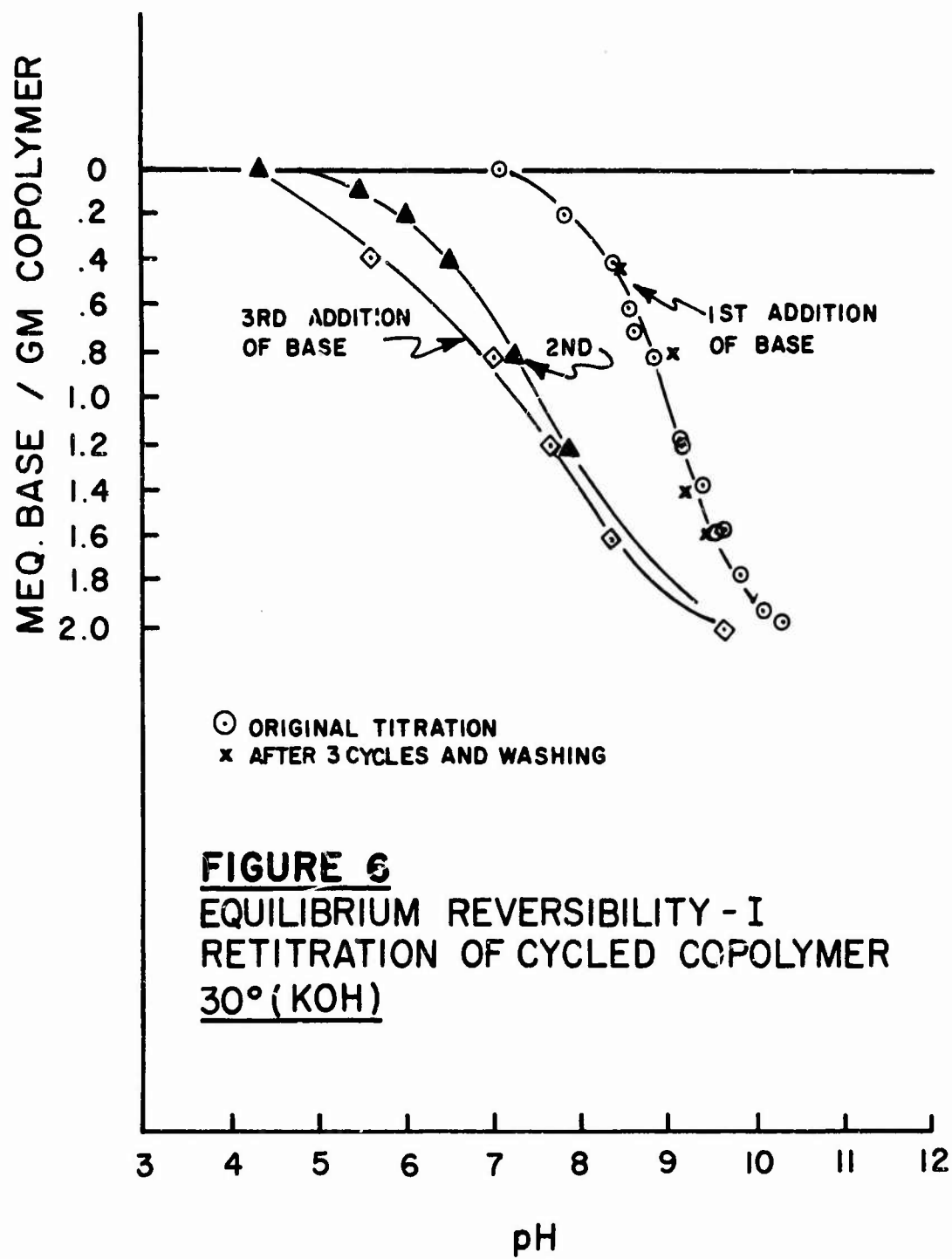
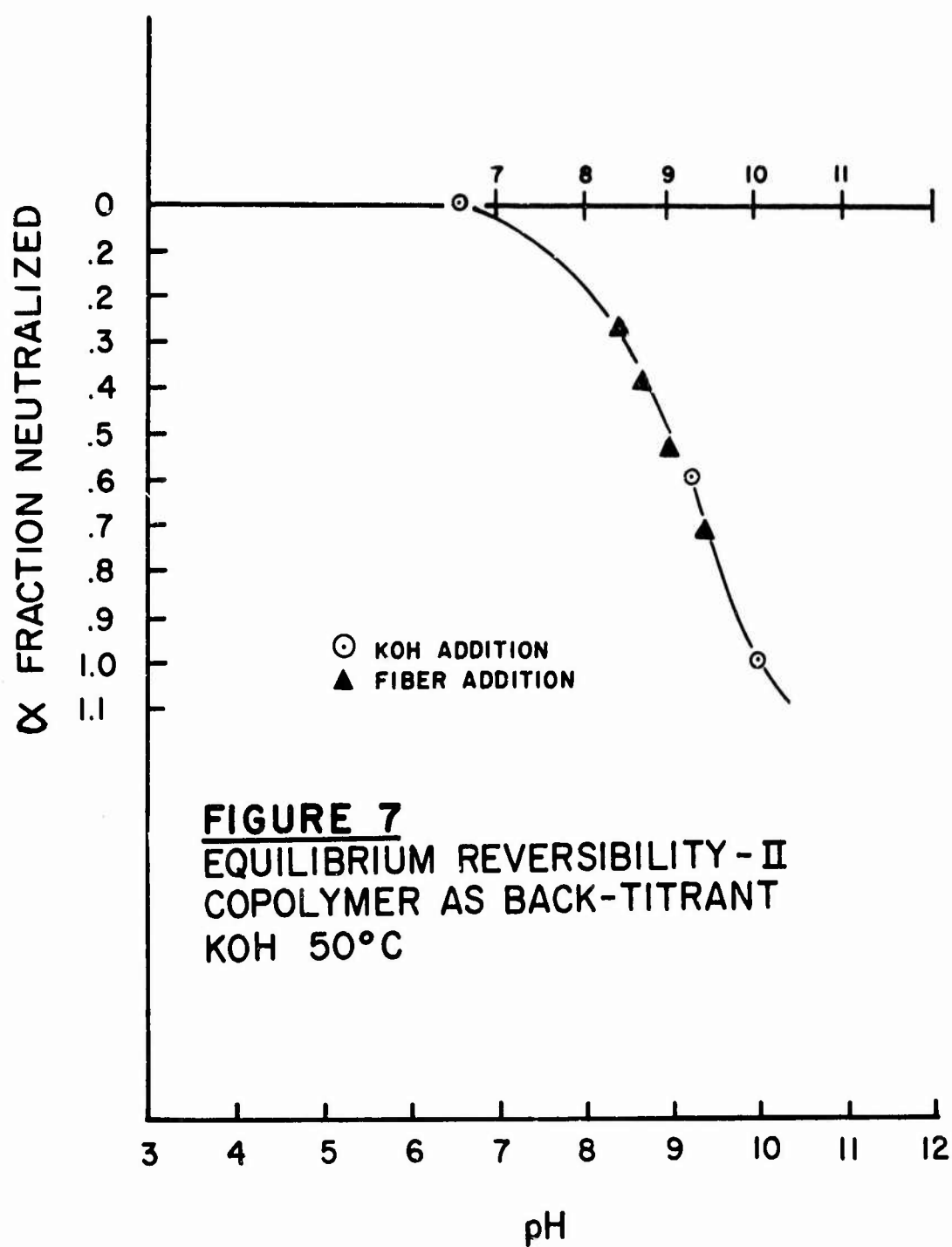


FIGURE 5
TITRATION OF
GRAFT COPOLYMER
WITH $\text{Ca}(\text{OH})_2$
(30°)







(7) Evidence of Conformational Transition

Early workers⁽¹⁶⁾ found that the behavior of weak organic acids could be described by the following expression:

$$\text{pH} = \text{pK}_a + \log \frac{(1-\alpha)}{\alpha}$$

where pK_a is a constant for the acid, and α is the fraction dissociated. An appropriate plot of the data for such acids, therefore, yields a straight line (Figure 8).

With polymeric acids, such as polyacrylic, a similar relationship is seen to hold:

$$\text{pH} = \text{pK}_a + n \log \frac{(1-\alpha)}{\alpha}$$

where n , the slope, is no longer equal to unity (Figure 8). This relationship derived by Henderscn and Hasselbach, was later applied⁽¹⁶⁾ to certain other polymeric acids, such as polymethacrylic. As shown in Figure 8, the curve for such an acid appears in two straight segments. This has been related to a picture of a gradual uncoiling of the polymer chains in solution, due to mutual repulsion of the carboxylate ions formed.^(16,17) The discontinuity found with such acids as polymethacrylic is attributed to an abrupt change in the conformation of the acid when a certain degree of dissociation is reached.^(17,19) The sharp change has been related to the presence of the pendant methyl groups, which presumably interfere with the free uncoiling (either by entangling or by mutual attraction in the polar medium) up to a point, then yield suddenly.

In either case, it would be predicted that the present copolymer acid, being much more hindered than polymethacrylic, should also show such a discontinuity. Titration data (Figure 9), for KOH at 30°C, show a distinct break. The apparent transition is seen to occur about pH 9, where (in the absence of added electrolyte) the copolymer acid is about half neutralized. This is the first reported observation of such a break in a solid (insoluble) polymer acid.

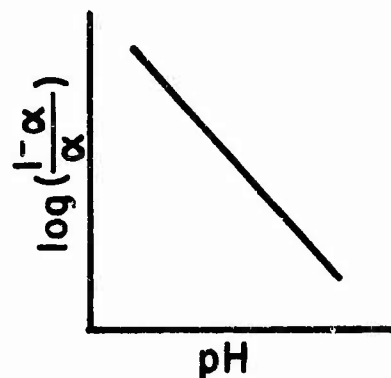
If the break in the curve is actually due to a rearrangement following the buildup of the charge on the anions, the presence of neutral electrolyte should minimize the repulsion between groups, and thus defer the transition to a point later in the titration, when a greater charge has been developed. Indeed, when the solution is 1M in KCl, the break does not occur until the acid is 95% neutralized (Figure 10). This is consistent with the picture of a morphological transition described above. (See Table II).

FIGURE 8 CONFORMATIONAL TRANSITION

1. Simple Acids (Organic)

$$\text{pH} = \text{p}k_a - \log\left(\frac{1-\alpha}{\alpha}\right)$$

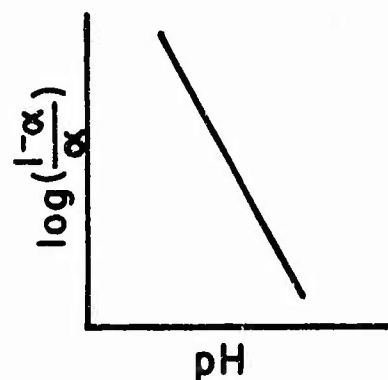
(Slope = 1)



2. Polymeric Acids (PAA)

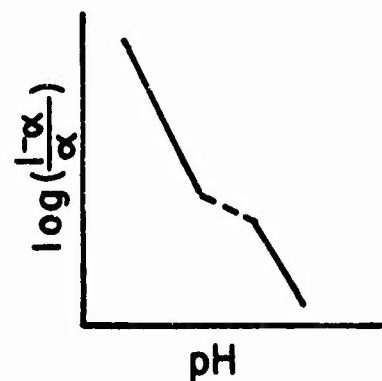
$$\text{pH} = \text{p}k_a - \frac{n}{\text{arrow}} \log\left(\frac{1-\alpha}{\alpha}\right)$$

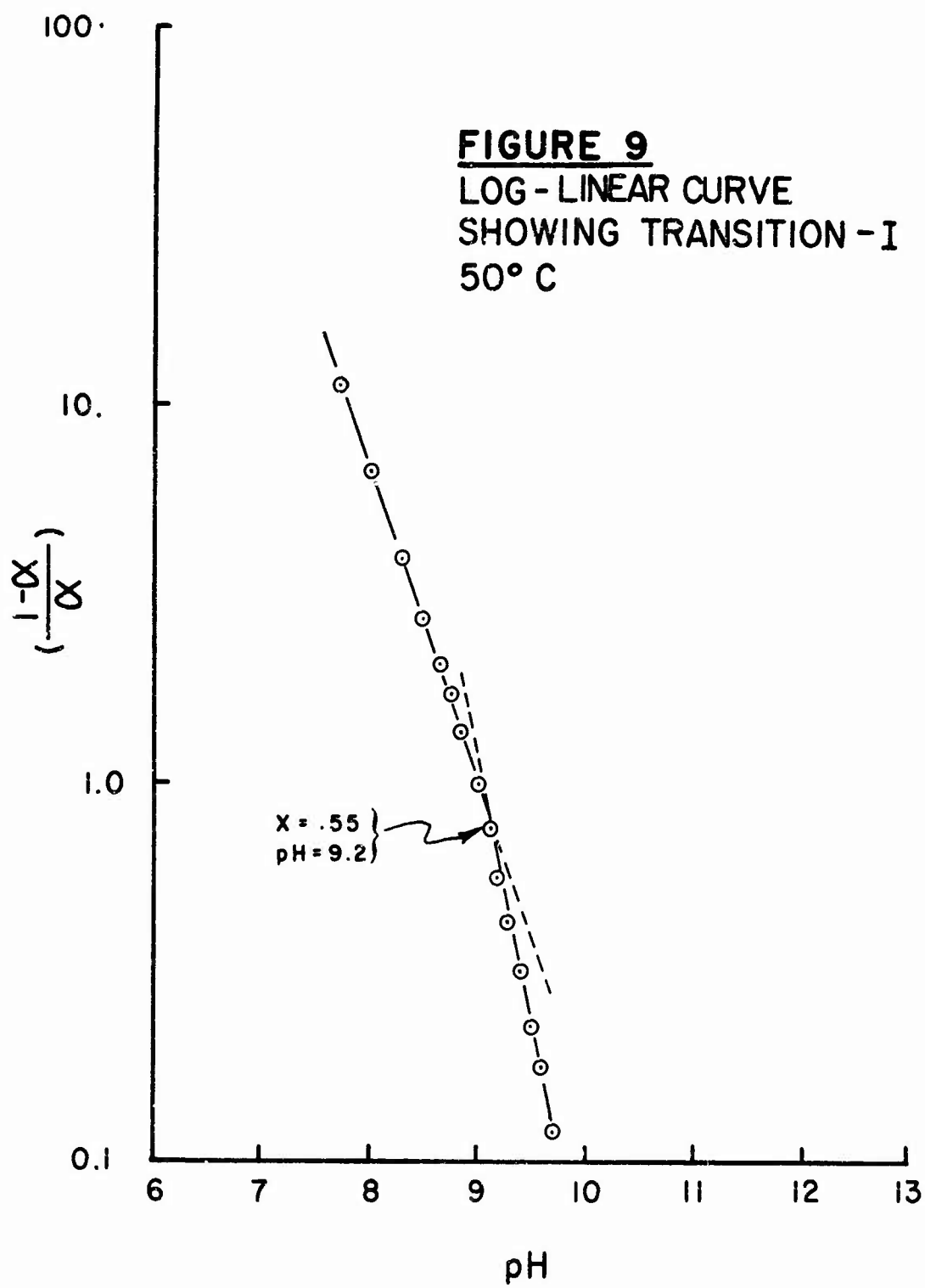
(Note: An arrow points to the 'n' in the denominator of the fraction, indicating it is a variable or specific to the polymer.)



3. Hindered Polymeric (PMA)

$$\text{pH} = \text{p}k_a - n \log\left(\frac{1-\alpha}{\alpha}\right)$$





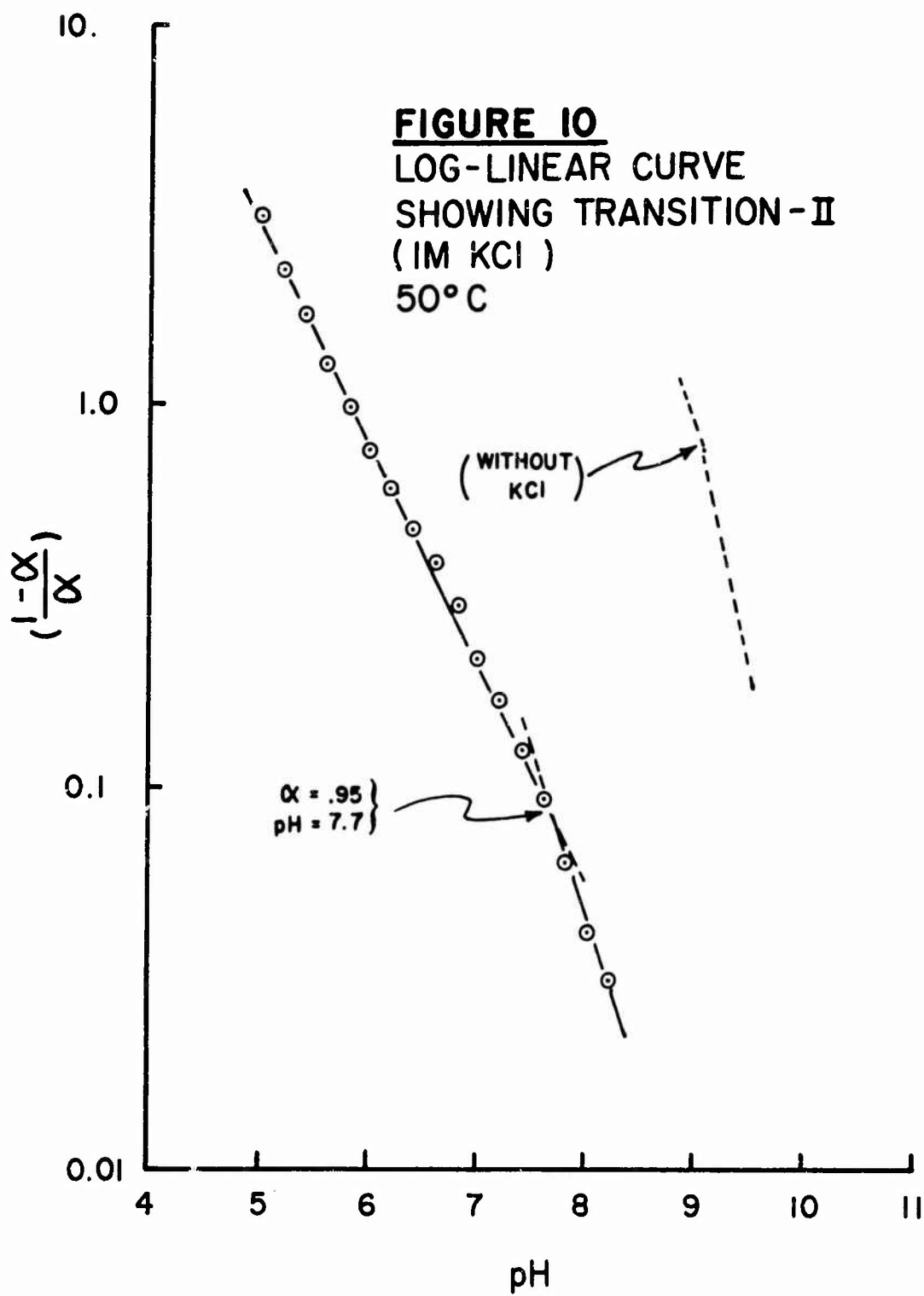


TABLE II
EFFECT OF TEMPERATURE AND ELECTROLYTE
ON CONFORMATIONAL TRANSITION

°C	KCl Conc.	pK _{app.}	Transition	
			pH	α
30°	--	9.0	9.2	.55
50	--	9.0	9.2	.55
50	.004 <u>M</u>	7.5	8.4	.75
50	1 <u>M</u>	5.8	7.8	.95

d. Titration with Strong Acid

Samples of the acrylic-modified nylon graft copolymer were prepared, as described above, and titrated with 0.1 N HCl. Although the inflection in the curve (Figure 2), as that for nylon 6.6 itself, is not clearly defined, the acid capacity (approximately .09 meq/gm) appears to be higher than the value typically reported for the backbone polymer (.05 meq./gm.)

Since the major modification of the polyamide involved its base-reactive capacity, work on acid reactivity was not carried further.

4. Summary and Recommendations

a. Summary

Significant equilibrium chemical characteristics of the nylon-acrylic acid graft copolymer may be summarized as follows:

(1) The base-reactive capacity of the graft copolymer (2.0 meq/gm) is about 20 times that of the base polymer nylon 6.6.

(2) The fiber has a very low apparent acid strength, probably related to the reduced mobility of the carboxylate acid groups. The value of pKa is affected by the size of the cation of the base used in the titration.

(3) A conformational transition apparently occurs at a characteristic pH. This is attributed to a shifting of polymer chains due to ionic repulsion.

(4) No significant change in equilibrium characteristics with temperature is observed.

(5) Neutral electrolyte in solution has a marked effect on both acid strength and transition region.

b. Recommendations

(1) In work where maximum base-reactive capacity toward a weak base is required, such as might be involved in work with toxic agent systems, neutral electrolyte might be utilized to increase effective acid strength where possible.

(2) The predictable correlation between the observed conformational transition and dimensional instability of fabrics made from this fiber should be established, and a program undertaken to increase dimensional stability by partially cross-linking or otherwise restraining the carboxyl groups further.

(3) For applications where maximum reactivity of carboxylic acid functional groups is required, graft copolymers having less closely packed acid groups should be considered.

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13. ABSTRACT		
<p>The radiation-grafted copolymer of acrylic acid on nylon 6,6 - a fiber with flash-resistant properties, was studied as representative of a new and useful class of textile fibers. The present report covers the first phase of research on the fundamental chemical properties of this fiber. Equilibrium characteristics are discussed and results of work on kinetics will follow.</p> <p>Equilibrium studies were made of rapidly-stirred suspensions of finely cut polymer fiber at several temperatures (30°-60°C). The base-reactive capacity (potassium hydroxide) was 2.0 milliequivalents per gram at 30°C (about twenty times that of the base polymer), with no significant change in capacity at higher temperatures.</p> <p>The acid strength of the copolymer was unexpectedly low (apparent pKa=9), an effect attributed to a heightened polyelectrolyte effect caused by restricted mobility of the carboxyl groups. Evidence for a conformational transition of the polymer chain at about 55% ionization was shown by a discontinuity in the Henderson-Hasselbach plot of the titration curve. This was attributed to a reversible shifting of the polymer chains. Neutral electrolyte caused a distinct increase in the apparent acid strength (pKa = 5.8), and a delay in the transition to a point later in the titration (95% neutralized). No effect of temperature on the equilibrium characteristics of the copolymer was observed.</p>		

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